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Reseñas

JEAN-SERVAIS STAS Atomic mass of the elements, phlorizin, and toxicology

JEAN-SERVAIS STAS Masa atómica de los elementos, florizina y toxicología.

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Abstract:

Jean-Servais Stas (1813-1891), a Belgium physician and brilliant analytical chemist, isolated (together witch de Koninck) phlorizin from the roots of wild apple, determined the physical and chemical properties of this new glucoside, and prepared the derivatives phloretin, phloretic acid, and phlorizein. The latter was proposed as a possible substitute of the dye orcein. Stas determined with Dumas the correct value of the atomic mass of carbon using carbon originating from three different sources: natural graphite artificial graphite, and diamond, and also determined the atomic mass of nitrogen, chlorine, sulfur, potassium, sodium, and silver and their relation to the atomic mass of hydrogen. The final results proved conclusively that Prout's hypothesis (all the atomic masses are multiples by a whole number of the atomic mass of hydrogen taken as 1) was wrong. Stas also showed that the composition of any given compound was independent of the procedure used for synthesizing it and that the ratio in which its elements combined to generate it was independent of the pressure and temperature. This principle also implied that the molecular mass of any compound was constant. Stas developed a new synthetic procedure for acetal and showed that Liebig's results were incorrect. Stas and Dumas gave a detailed explanation of the action of KOH on alcohols and their main ethers and provided chemists with a simple tool to synthesize the equivalent acid. Stas showed that it was possible to detect ingested arsenic in animal tissues, as well as detect in a suspected liquid the presence and identity of all the known alkaloids (e.g. coniine, nicotine, morphine, codeine, noscapine, strychnine, brucine, cevadine, colchicine, delphin, emetine, solanine, aconitine, atropine, hyoscyamine, etc.), in whatever state they were present.

Keywords: analytical chemistry, arsenic, atomic mass, phlorizin, Prout's hypothesis, toxicology.

Resumen:

Jean-Servais Stas (1813-1891), fue un médico belga y brillante químico analítico que con de Koninck separó la florizina de las raíces del manzano silvestre, determinó las propiedades físicas, y químicas de este nuevo glucósido y preparó los derivados floretina, ácido florético y and florizeína. Esta última fue propuesta como un posible substituto de la tintura orceina. Junto con Dumas determinó el valor correcto de la masa atómica del carbono usando carbón de tres fuentes: grafito natural, grafito artificial y diamante, y también determinó las masas atómicas del nitrógeno, cloro, azufre, potasio, sodio, y la plata y su relación relativa a la masa atómica del hidrógeno. Los resultados finales demostraron en forma inequívoca que la hipótesis de Prout (todas las masas atómicas son múltiplos enteros de la masa atómica del hidrógeno considerada como 1) estaba equivocada. Stas también demostró que la composición de cualquier compuesto era independiente del proceso usado para sintetizarlo y que la razón en la cual los elementos se combinaban para generarlo era independiente de la presión y la temperatura. Este principio también implicaba que la masa molecular de un compuesto era constante. Stas propuso un nuevo método de síntesis del acetal y demostró que los resultados de Liebig eran incorrectos. Stas y Dumas desarrollaron una detallada explicación de la acción del KOH sobre los alcoholes y sus principales éteres, y proporcionaron a los químicos con una herramienta simple para preparar el ácido equivalente. Stas demostró que era posible detectar arsénico en tejidos animales, así como detectar en un líquido sospechoso la presencia e identidad de todos los alcaloides conocidos (e.g. coniina, nicotina, morfina, codeína, noscapina, estricnina, brucina, cevadina, colchicina, delphin, emetina, solanina, aconitina, atropina, hyoscyamina, etc.), en cualquier estado que estuvieran presentes.

Palabras clave: arsénico, florizina, hipótesis de Prout, masa atómica, química analítica, toxicología.

INTRODUCTION

Life and career (Morley, 1892; Spring, 1894; Timmermans, 1938)

Jean-Servais Stas (Figure 1) was born on August 21, 1813 in Leuven, Belgium, the third of the eight children of Jean-Baptiste Stas, a prosperous locksmith and stove maker, and Jeanne-Josèphe De Mortier. He received his basic education first at a private school and then at the community college. Afterwards he enrolled in the Faculty of Philosophy and Faculty of Medicine of the University of Louvain and received his medical degree with distinction in 1835. Shortly thereafter the political and religious unrest led to the suppression of the university. Upon graduation he was appointed assistant to Jean-Baptiste Van Mons (1765-1842); in this position he published his first paper about phlorizin (Stas & de Konick, 1835). In 1837 Stas moved to Paris and begun working in the laboratory of Jean-Baptiste Dumas (1800-1884) at the École Polytechnique continuing his research about phlorizin (Stas, 1838, 1839). Simultaneously he worked with Dumas on the action of KOH on alcohols, the application of the type theory to the property of hydrogen of substituting chlorine in chloro alkanes, and, particularly, on the determination of the molecular mass of carbon dioxide, and consequently, the true atomic mass of carbon and rejection of Prout's hypothesis. Determination of the atomic mass of carbon would lead him to a lifetime project on the correct atomic masses of the elements, rejection of Prout's hypothesis, and thence, academic and international fame (Morley, 1892; Spring, 1894; Timmermans, 1938). In 1840, Stas was appointed to the chair of chemistry at the École Royale Militaire in Brussels, a position he kept until 1869, when he was forced to resign because of problems with his voice caused by a larynx ailment, and before serving the thirty years necessary to secure a pension. Jean Servais died in Brussels and was buried at Leuven.

Stas received many honors for his research and public work. He was member of the Institut de France, honorary member of Académie Royale de Médecine de Belgique; member of the Académie Royale des Science et Belles-Lettres de Bruxelles (1841) and its President in 1890; member of the Chemical Society of London, of the Académie Royale de Bavière, of the Académie de Médecine of Stockholm, of the Société Royale des Sciences of Turin, of the German Chemical Society, and of the American Chemical Society; foreign member of the Royal Society of London (1879), and corresponding member of the Société Royale des Sciences de Göttingen. He was also member of the Conseil de Salubrité Publique d'Ixelles (1846), member of the international committee of the International Expositions in London (1862) and Paris (1865), Belgium's representative at the monetary conference of 1867, president of the Belgium commission of weights and measure, President of the International Meter commission (1872), President of the conference of the meter (London, 1874), member of the commission of the Royal Observatory of Belgium (1877) and member of its directing committee (1883-1885); technical councilor of the Belgium National Bank, commissioner of the Mint but resigned in 1872 because he disagreed with the government's monetary policy (Morley, 1892; Spring, 1894; Timmermans, 1938).

He was nominated doctor honoris causa of the University of Bonn (1868) and of the University of Leyden (1874), and in 1885 he was awarded the Davy Medal from the Royal Society and the Copley Medal from the Royale Chemical Society of London for his researches into atomic masses. He was elected to the Légion d'Honneur, Grand Officier of the Belgian Order of Leopold, and knight of many European orders (Morley, 1892; Spring, 1894; Timmermans, 1938).

Scientific contribution

Stas wrote about 45 papers (several of them longer than 150 pages), booklets and books in the areas of inorganic, organic, and analytical chemistry, atomic masses, spectroscopy, platinum alloys, Prout's hypothesis, toxicology, etc. A 3-volume book of over 2300 pages containing all his writings was published posthumously (Stas, 1894a b c). In addition to the subjects discussed below, Stas studied the action of hydrogen upon chlorinated compounds (Stas, 1841), the composition of air (Stas, 1842), the action of sulfuric acid upon acetic acid (Stas & de Hemptinne, 1843), the composition of the amniotic and allantois fluids (Stas, 1850), the action of chlorine on silver carbonate (Stas, 1867b), the manufacture of glass for chemical vessels (Stas, 1868a), the preparation of iodic acid and potassium iodate (Stas, 1868b), the action of SO. on silver compounds (Stas, 1868c), chemical statics (Stas, 1871), the relation between science and human curiosity (Stas, 1880), the nature of solar light (Stas, 1889-1893a), silver (Stas, 1889-1893b), spectroscopy of simple bodies (Stas, 1889-1893c), etc.

Phloridizin

In 1835 Laurent Guillaume de Koninck (1809-1887) and Stas informed the Académie Royal de Sciences of Brussels that they had discovered a new substance in the roots of the wild apple, pear, plum, and cherry trees, which they had named *phlorizin*, from *floioa*, bark, and *riza*, root (Stas & de Koninck, 1835). Pure phlorizin was a yellow white material, crystallizing in the form of silky needles, initially bitter and then astringent, little soluble in cold water and more in hot water, very soluble in alcohol and ether, soluble in concentrated sulfuric acid and HCl without decomposition, and without action on litmus paper and violet syrup. It dissolved in concentrated nitric acid yielding a yellow precipitate, turned dark brown an aqueous solution of ferric sulfate, produced a white precipitate with lead acetate, silver nitrate, and chlorinated water, and did not react with ammonia, limewater, mercuric chloride, emetic tartar (antimony potassium tartrate), and strong glue (Stas & de Koninck, 1835). A following publication by Stas provided a detailed description of the experimental procedure for extracting phlorizin from the bark, the properties and composition of the glucoside, and several of its derivatives (Stas, 1838).

In a first procedure, phlorizin was obtained by boiling for several hours a concentrated aqueous mixture of the roots of apple tree, leaving the broth to cool in a fresh environment, separating the silky crystalline precipitate and purifying it with animal charcoal. Stas found that this procedure was only appropriate for the preparation of small amounts of the glucoside. Treatment of larger amounts of the bark resulted in the extraction of a series of other substances, particularly one colorless, non-crystallizable and extremely astringent, which rapidly absorbed oxygen from the air and turned into a red resin, was sparingly soluble in water and very soluble in alcohol, and prevented the crystallization of phloridzin. To avoid this problem it was better to extract the fresh or dry bark of apple tree roots for several hours with diluted ethanol at 50. to 60.C. The alcohol was then separated by distillation, the residue cooled to atmospheric temperature, and the colored precipitate purified with animal charcoal (Stas & de Koninck, 1835).

The phloridzin prepared by both procedures had the same properties: white silky crystalline material, shaped as long fine needles, sparingly soluble in water and boiling ether, very soluble in ethanol, methanol, and a mixture of alcohol and ether. An elemental analysis indicated that it contained by weight 53.8 to 54.2% carbon, 6.0 to 6.2% hydrogen, and 39.8 to 40.1% oxygen, corresponding to the global formula $C_{64.42.18}$ (using 75 as the atomic mass of carbon and 100 for that of oxygen; the correct composition and formula are 57.79% carbon, 5.54% hydrogen, 36.66% oxygen; $C_{21.24.10}$). Phlorizin heated to 100.C lost its crystalline aspect while releasing water; it begun melting at 106.C and became totally liquid at 109.C. At higher temperatures it began to solidify and then turned in a hard substance looking like Arabic gum. At 160.C it liquefied again and remained in that state up to 200.C when it began to boil, releasing more water and turning dark red; total decomposition took place at about 350.C. Stas reported that treatment of the body obtained at about 160.C with mineral acids (e.g. sulfuric, phosphoric, HCl, and HI) decomposed it into phloretin (the aglucon of phlorizin) and grape sugar (glucose). According to Stas his results indicated that the elemental composition of anhydrous phlorizin corresponded to the formula $C_{64.30.12}$ (Stas, 1838).

The following section described phloretin as a sweet white crystalline solid, sparingly soluble in cold water, a little more soluble in boiling water and boiling ether, totally soluble in methanol, ethanol, and boiling glacial acetic acid, melting at 180.C, and decomposing completely at higher temperatures. It was decomposed by nitric acid, chromic acid converted it into formic acid and CO., and it absorbed about 14% of its weight of ammonia gas. Elemental analysis indicated that it contained, by weight, about 66.2% carbon, 4.9% hydrogen, and 28.9% oxygen, corresponding to the formula $C_{48.22}O$. (the correct composition and formula are 65.69% carbon, 5.15% hydrogen, 29.17% oxygen; $C_{15.14}O$.) (Stas, 1838).

Stas studied in detail the influence of nitric acid and ammonia on phlorizin. The cold diluted acid dissolved phlorizin initially without changing it, and afterwards, destroying it completely. Concentrated nitric acid decomposed phlorizin immediately into NO., CO., oxalic acid, and a dark red substance, which Stas named *phloretic acid*. The latter was a non-crystallizable substance, decomposing at about 150.C, insoluble in water, soluble in ethanol, ethanol, and alkalis, insoluble in diluted acids, and soluble in concentrated sulfuric acid. Ammonia gas attacked phlorizin converting it into a blue ammonium salt of a red coloring substance that Stas named *phlorizein*, containing, by weight, about 46.0% carbon, 5.8% hydrogen, 6.6% nitrogen, and 41.6% oxygen. Phlorizein was a non-crystallizable, non-volatile, and infusible solid, slightly bitter, soluble in boiling water, slightly soluble in ethanol, methanol, and ether, and completely destroyable by chlorine (Stas, 1838). In another publication Stas suggested the possibility of using the blue ammonium salt as dye replacing orcein (Stas, 1839).

ATOMIC MASS OF CARBON

In their first paper on the subject Dumas and Stas remarked that the combination or the exchange of substances occurred under certain numerical ratios that constituted the basis of modern chemistry (Dumas & Stas, 1840c, 1841). Their results indicated that there was an error of about 2% in the determination of the amount of carbon, which expressed the ratio by which carbon united with other natural substances. This error was so serious that it required changing the accepted values of the atomic masses of simple bodies and the formula of an immense number of chemical combinations. For example, the composition of cholesterol, instead of being, by weight, 85% carbon, 12% hydrogen, and 3% oxygen, should be 83% carbon, 12% hydrogen, and 4.5% oxygen; thus changing by near 50% the proportion of the oxygen. In its most simple form, the question was if in the production of CO. oxygen and carbon combined in the mass ratio 800 to 306, as postulated by Berzelius, or 800 to 300, as Dumas and Stas results seemed to indicate. If a chemist found that the analysis of 100 parts of any substance yielded 3614 parts of CO., then, according to Berzelius, he had to conclude that the substance was pure carbon or that it contained at least 1.5% of oxygen, hydrogen, or other bodies. This was a common error done in the analysis of anthracites or pit coal, which had been reported recently in the literature. The elemental composition of a substance was normally determined from the results of its total combustion, that is, its transformation into water and CO.. The amounts of carbon and hydrogen present were easily calculated from the weights of substance burned and the weights of water and CO. produced. Normally, the amount of carbon and hydrogen thus determined exceeded the amount of the original substance. For example, using this procedure Dumas had found that naphthalene contained, by weight, 95.5% carbon and 6.1% hydrogen, for a total of 101.6 instead of 100. In the case of benzene, he had obtained 93.5% carbon and 7.7% hydrogen, which made 101.2 instead of 100. According to the substitution theory, chlorine reacted with organic compounds replacing one volume of hydrogen for each volume of chlorine attached. Application of this rule to naphthalene required that its composition by weight be 94% carbon and 6% hydrogen, figures different from the ones obtained by combustion. These anomalies indicated that the substitution theory was wrong or that there was an error in the analysis of water and CO.. Since all chemists had accepted the substitution theory and the composition of water was well established, the only thing left was to verify the elemental composition of CO. (Dumas & Stas, 1840c, 1841).

Dumas and Stas followed a very simple procedure for determining the elemental composition of CO.: Burning a known weight of pure carbon in oxygen and weighing the CO. thus formed. They made 14 experiments using carbon originating from three different sources (a) natural graphite (from Ceylon) taken from the collection of the *Jardin du Roi* (afterwards, *Jardin des Plantes*); (b) artificial graphite extracted from a ferruginous mass produced in a high furnace; and (c) diamond (Dumas & Stas, 1840c, 1841).

The paper described in extreme detail the procedure used to clean the graphite from all possible oxidizable impurities. The clean graphite, contained in a platinum tray, was placed in a 1-meter long tube made of very hard glass. A mixture of copper oxide and potassium chlorate provided the oxygen required. The gas produced was passed over pure copper oxide, strongly heated to destroy all the carbon monoxide, which could be produced. The combustion gases were weighted using Jean-Baptiste Boussingault's (1802-1887) procedure for analyzing air (Boussingault, 1834): the gases are passed through tubes filled with small pieces of pumice stone, moistened with sulfuric acid when it was required to retain water, and with potash when it was required to absorb CO.. After having been filtered through the pores of the pumice stone thus prepared, the gases passed out perfectly free from water or CO. (Dumas & Stas, 1840c, 1841).

The two varieties of graphite gave the same results and were found not to contain hydrogen. The results indicated that during the combustion of graphite, natural as well as artificial, 800 parts of oxygen combined with 300 of carbon to form 1100 of carbonic acid. Nevertheless, Dumas and Stas pointed out that the mean of the nine experiments conducted was 800 to 299.93.

All the diamonds burned left a considerable residue consisting, sometimes of a spongy mater of a yellowish-red tint; sometimes of yellow crystalline flakes; and in others, of colorless crystalline fragments. These residues belonged essentially to the diamond crystal itself and had been imprisoned within it at the time of its formation, providing thus a fingerprint of the geological source of each stone. Dumas and Stas found that the amount of the residue varied from 1 part in 2000 to 1 in 500. The combustion procedure and apparatus were slightly modified to assure complete combustion of the diamonds. The glass tube was replaced by one made of porcelain where the carbonaceous matter was heated to incandescence by means of a stream of pure and dry oxygen. The gas was bubbled through washing bottles containing limewater, a tube full of pumice-stone saturated with aqueous KOH, and over other flasks containing pieces of glass covered with sulfuric acid, and finally, through a tube filled with pumice stones in grains, moistened with boiled sulfuric acid. All these absorbing pieces were of appropriate dimensions to assure complete absorption of the pertinent gas (Dumas & Stas, 1840c, 1841). The results of five experiments indicated that during the combustion of diamond, 800 parts of oxygen combined with 300 of carbon to form 1100 of carbonic acid, with an average of 300.02.

The paper contains a table detailing the weight of the sample and of CO. produced, and the ratio between these two quantities, as well as the resulting value 75.005 for the atomic mass of carbon (oxygen =100), against 76.52 proposed by Berzelius (Dumas & Stas, 1840c, 1841).

Dumas and Stas remarked that their experiments seemed to confirm William Prout's (1785-1850) hypothesis that all atomic masses were multiples of that of hydrogen by whole numbers (later on Dumas and Stas would reject this hypothesis). According to Prout the atomic mass of charcoal was exactly equal to six times that of hydrogen, or 12.5 X 6 = 75, which was equal to the mean of Dumas and Stas' results. Thus, 1 part of hydrogen combined with 8 parts of oxygen to form water, and with 3 parts of carbon to form methane, or marsh gas, and consequently, 8 parts of carbon combined with 3 of oxygen to form CO. (Dumas & Stas, 1840c, 1841). Dumas and Stas ended their paper describing the possible sources of the errors committed when using the standard method of combustion and the means to eliminate them.

In a following publication Stas mentioned that many scientists had criticized the value 75.00 for the atomic mass of carbon and calculated other values using the law of ideal gases, the value of the density of gases such as carbon monoxide, carbon dioxide and oxygen, the combustion of a series de silver salts (e.g. acetate, tartrate, paratartrate, and malate), etc. Against these arguments Stas mentioned that Victor Regnault (1810-1878) had shown that the behavior of carbon dioxide deviated strongly from ideal already at 0.C; silver volatilized strongly at the combustion temperature of its salts, silver tartrate prepared by reacting tartaric acid with silver nitrate always contained traces of silver nitrate, etc. etc. To dissipate all doubts Stas decided to calculate again the value of the atomic mass of carbon using this time the oxidation of carbon monoxide to carbon dioxide. In his paper he gave a detailed description of the equipment used and all the measures he took to assure that his two reagents (carbon dioxide and oxygen) were dry and as pure as possible. Carbon monoxide was prepared by treating oxalic acid dried at 100.C with three times its weight of fuming sulfuric acid. A series of washing bottles containing aqueous KOH, pieces of pure KOH, pumice stone wet with KOH, and pumice stone wet with sulfuric acid, were used to eliminate possible traces of the CO. contained in the carbon monoxide. Similar arrangements were used to purify the oxygen prepared by reduction of copper oxide. Once again, the results of nine experiences indicated that the atomic mass of carbon was 75.00 (Stas, 1849).

Atomic masses - reciprocal relations

In 1860 Stas published a long memoir reporting the results of his investigation about the validity of Prout's hypothesis that all the atomic masses were multiples by a whole number of the atomic mass of hydrogen taken as 1. In this work he determined the atomic masses of nitrogen, chlorine, sulfur, potassium, sodium, and silver and their relation to the atomic mass of hydrogen. He selected these elements because they were very well known, their compounds were stable, and most people believed they followed Prout's law. He mentioned that in every case he had made two determinations, which allowed him determine the atomic mass in relation to that of oxygen. The pertinent analyses were made by direct synthesis of a given compound or the result of a double decomposition. He also mentioned that *the only way to make accurate measurements and determine exactly small differences, was to use large quantities of the reagents, so as to make the these differences substantially larger than the errors made in the observations* (Stas, 1860).

The paper was divided in two sections. The first one described the equipment (balances, weights, and vases), the chemicals used (distilled water, HCl, nitric acid, sulfuric acid, ammonium chloride, and sodium carbonate), and the preparation of highly pure silver. The second part described the synthesis of silver chloride, sulfide, and nitrate, lead nitrate and sulfate, the analysis of potassium chlorate and silver sulfate, the determination of the proportional ratio between silver and potassium chloride, sodium chloride, and ammonium chloride, of silver nitrate and potassium chloride, ammonium chloride, etc. (Stas, 1860).

The following examples will illustrate the extreme care taken by Stas to ensure the purity of the substances employed, the accuracy in the weightings, and the maximum elimination of error sources. For weighing purposes he used four balances (built by the best European technicians) and two sets of weights. The largest balance had a capacity of five to six kilos in each plate and a difference in weighing of one milligram. The second balance had capacity of 500 grams in each plate and allowed determining a weight difference of 0.2 mg. The third balance had a capacity of 25 g in each plate and detected a difference of 0.033 mg. The fourth balance had a capacity of one kg in each plate and detected a difference of 0.5 mg. Stas believed that no one owned a set of balances of such capacity and accuracy. Two sets of weights were employed, one of platinum and the other of brass; those of platinum started at 1 kg and went down to 0.5 mg. When practical, all the vessels used were made of platinum (Stas, 1860).

Inspection of the methods available for the preparation of pure silver indicated that in the end, all of them left one or more impurities. For example, all those based on the reduction of silver chloride provided silver containing copper and iron. Stas developed many other alternatives, among them, reacting phosphorus finely divided with an aqueous solution of silver nitrate diluted to 1/100. The precipitated silver was then left in contact with a solution of silver nitrate, afterwards digested with an aqueous solution of ammonia, and finally fused with a mixture of highly pure potassium nitrate and borax. This was a very slow process but produced extremely pure silver (Stas, 1860).

The synthesis of silver chloride was carried on by several methods, for example, heating silver in a stream of chlorine; dissolving the silver in nitric acid, precipitating the resulting silver nitrate with gaseous HCl, followed by evaporation in the same vase, and melting the chloride obtained in an atmosphere of HCl; dissolving the silver in nitric acid, precipitating the nitrate with a solution of ammonium chloride, fusing the salt in an atmosphere of HCl, and evaporating everything in the absence of air; etc. Stas provided a table describing the results of the three experiments he conducted with silver and dry chlorine: For 100 g of silver he obtained 132.841, 132.843, and 132.843 g of silver chloride, respectively. Similar descriptions were given for the preparation of silver nitrate, silver sulfide, potassium chloride, sodium chloride, pure lead, lead nitrate, lead sulfate, etc. (Stas, 1860).

The final results indicated that Prout's hypothesis was incorrect: the twelve salts studied gave a ratio different from the one calculated according to Prout. For example, Prout predicted that the ratio of atomic masses between silver and chlorine should 100 to 32.87; Stas results indicated a ratio of 100 to 32.8445. For silver sulfide Prout predicted 100 to 14.814 against Stas' results of 100 against 14.852. The values of atomic masses used at the time were also different from the ones calculated from Stas' experiments, taking oxygen as 8 (Stas, 1860):

Stas now rejected Prout's hypothesis stating "as long as establishing the laws that govern matter we must adhere to experience, we must consider Prout's law as a pure illusion, and regard the non-decomposable bodies of our globe as distinct beings having no relation one to the other. The incontestable analogy of properties observed in certain elements must be sought for in other causes than those derived from the ratio of the weight of their acting masses" (Stas, 1860).

In a following publication Stas repeated his claim that the composition of any given compound was independent of the procedure used for synthesizing it and that the ratio in which its elements combined to generate it was independent of the pressure and temperature. This principle also implied that the molecular mass of any compound was constant. He determined the atomic masses of several elements and reported them in relation to hydrogen and oxygen, as follows (Stas, 1866, 1867a):

Acetal

In 1832 Johann Wolfgang Döbereiner (1780-1849) reported that the reaction between ethanol vapor and air in the presence of platinum black produced a particular liquid, which he named *sauerstoffaether* (oxygenated ether). Oxygenated ether was a colorless flammable liquid, smelling like ethyl nitrate, having relative density 0.842 at 21.C, vapor pressure 333.5 mmHg at 75.C, and transforming into acetic acid under the continuous action of platinum black (Döbereiner, 1832). Justus von Liebig (1803-1883) repeated Döbereiner's procedure using manganese dioxide as the oxidizing medium, analyzed the product boiling at 95.2.C, and found it contained, by weight, 59.72% carbon, 10.97% hydrogen, and 29.31% oxygen, corresponding to the formula $C.H_{18}O.$ (using 75.0 and 12.5 as the atomic masses of carbon and hydrogen, respectively; the correct composition and formula are 60.98% carbon, 11.94% hydrogen, 27.08% oxygen; $C.H_{14}O.$). He changed the name of this new substance to *acetal*, believing it gave a better idea about its being as intermediate product during the formation of acetic acid (Liebig, 1833).

According to Stas, acetal was usually considered to be a combination of ether and aldehyde, or as formed by two molecules of ether where one of them had lost one atom of hydrogen and gained one atom of oxygen (Stas, 1847). He believed that the composition reported by Liebig was in error and for this reason he decided to investigate acetal in more detail. He followed Liebig's procedure in detail and obtained a product, which, when redistilled, did not possess any fixed boiling point. Redistillation of the liquid fraction passing at 95 °C showed that it began boiling at about 88°C and continued to do so up 108° to 110 °C. The fraction distilled at 88 °C was reduced to about half by a concentrated solution of potash without the contact of air. The portion collected at about 104 °C, and below, did not undergo any appreciable alteration by an alkaline solution in the absence of air. To Stas, these facts proved that the acetal described by Liebig was a mixture of at least two substances, one of which was acetic ether, and the other acetal, properly so called, and comparable to the *methylal* of Faustino Jovita Malaguti (1802-1878) (Malaguti, 1838; Stas, 1847).

The next step was the development of a faster and more efficient method for preparing acetal. The first stage of Stas' process consisted in washing fragments of pumice stone with HCl, followed by heating them to redness and then moistening with ethanol almost anhydrous. The pumice stone was then put on the bottom of flask of about 45 to 50 liters capacity, and the flask filled with as many as possible flat glass capsules covered with a thin layer of platinum black. The flask neck was now covered with a glass plate and the whole exposed to a temperature of about 20°C until nearly all the alcohol converted into acetic acid. One to two liters of alcohol of 60% were now added, the flask neck covered again, and everything left at 20.C for about 15 to 20 days, while occasionally admitting fresh air into the flask. The resulting liquid was removed and the whole process repeated as many times as desired. The accumulated liquid was neutralized by potassium carbonate and then saturated with calcium chloride. This solution was distilled cautiously, recovering only the first quarter passing over. Saturation of the distillate with fused calcium chloride separated a considerable portion of a very volatile fluid of an extremely suffocating odor. Further purification gave acetal as a colorless ethereal and fluid liquid, having a peculiar sweet smell, relative density 0.821 at about 22.4 °C, boiling between 104° and 106 °C, partly soluble in water, and completely soluble in ether and alcohol (Stas, 1847).

Acetal could be kept in dry or humid air, without alteration. In the presence of platinum black it very rapidly converted, first into aldehyde and then into concentrated acetic acid; the reaction was extremely rapid when the platina was moistened; the same result was obtained with oxidizing bodies such as diluted nitric and chromic acids. Elemental analysis indicated that acetal contained, by weight, 61.01% carbon, 11.85% hydrogen, and 27.14% oxygen, corresponding to the formula $C_{12.14}O$.. Consequently, acetal could be represented by a combination of two molecules of ether with one molecule of aldehyde, $C_{12.14}O. = 2(C.H.O)$, C.H.O., which easily explained its transformation into aldehyde and acetic acid (Stas, 1847).

Action of alkalis on alcohols

In a short communication published in 1840 Dumas and Stas reported that alcohols, under the influence of KOH and heat, transformed into pure hydrogen and the pure corresponding acid (same chain length). Thus methanol, ethanol, ethal (cetylic alcohol), and amyl alcohol (fusel oil) converted into pure hydrogen and pure formic acid, acetic acid, hexadecanoic acid, and valeric acid, respectively. In other words, during this transformation the alcohol lost four volumes of hydrogen and won two of oxygen, in accordance with the theory of types and the law of substitution. They also reported that glycerin also provided pure hydrogen, although they had been unable yet to separate the resulting acid (Dumas & Stas, 1840a).

Dumas and Stas believed these results allowed and easy explanation of the action of anhydrous baryta (barium oxide) on alcohol. The results of their experiments indicated that this reaction produced three to four different gases: (1) olefiant gas (ethylene), which was absorbed in fuming sulfuric acid and converted by chlorine into Dutch liquor (ethylene dichloride); (2) swamp gas (methane), which remained after ethylene had been absorbed by sulfuric acid, and chlorine converted into the corresponding chloride; (3) hydrogen; and (4) carbon monoxide. These three gases originated as followed: (a) anhydrous baryta reacted with the alcohol giving barium hydroxide and ethylene; (b) barium hydroxide reacted with alcohol producing hydrogen and barium acetate; (c) barium acetate, in the presence of an excess of base, furnished methane and barium carbonate (Dumas & Stas, 1840a).

In a following publication Dumas and Stas gave a more detailed explanation of the action of KOH on alcohols and their main ethers, as well providing chemists with a simple tool to synthesize the equivalent acid in a large number of cases. In addition to the action of KOH on a series of alcohols, they described the preparation and properties of the corresponding acids, their salts, ethers, and derivatives, for example, valeric acid, chlorovaleric acid, silver valerate, pyroacetic ether (acetone), oxalic ether, benzoic ether, methylethyl ether, dimethyl ether, ethal (cetyl alcohol), potassium ethalate, etc. (Dumas & Stas, 1840b).

Nicotine poisoning

Stas was called in many opportunities to perform legal pathological exams. The most notorious was probably the one related to the Bocarmé affair. The count Hyppolyte Visart de Bocarmé had married a woman from the bourgeoisie, heiress to a large fortune, which she shared with her sickly brother Gustave Fougnies. When the brother announced his intentions of getting married the count saw his economic future menaced and decided to murder his brother-in law using an undetectable poison (nicotine)*, and declare that the death was caused by a heart attack. During a dinner in the castle, a fight took place between the count and Fougnies during which the latter fell to the floor and there the count administered him the poison. Part of the potion fell on the clothes of the victim and on the floor. The public opinion believed a crime had been committed and the court was forced to order an autopsy of the body (Stas, 1851).

On November 27, 1850, Stas received an order from the examining judge Bemelmans to conduct a chemical analysis of parts of the body of Gustave Fougnies and verify if the deceased (a) had ingested any poisonous or morbid substance, in particular, sulfuric acid; (b) the nature of and amount of the same; (c) if this substance was in a liquid state at the time of the ingestion, and (d) if the black color of the lower lip, the tongue, the mucosa and the posterior of the mouth, and the pharynx, was due to the passage of a particular acid, notably sulfuric. The order was accompanied by four jars containing the lung, stomach, intestines and the liquid contained in the same, the liver, the spleen, the tongue, the lower jaw, the back of the mouth, and the larynx of the deceased (Stas, 1851).

A detailed physical examination of the tongue and the stomach and its contents, showed the presence of substantial amounts of acetic acid only and no signs of sulfuric acid or other mineral acids. The alterations present in the tongue could well be due to the ingestion of concentrated acetic acid; the tongue, back of the mouth, and larynx were found to exhale a strong odor of acetic acid (vinegar) and turn litmus paper strong red. Stas went on to investigate the presence of vegetable alkalis. The first essays showed the absence of morphine, strychnine and brucine. Addition of an aqueous solution of KOH on a small amount of the liquid, released an animal and sickening smell; this result, together with the acrid state of the liquid, suggested Stas the possible existence of a volatile alkaloid. Further examination showed that the liquid contained an oily substance smelling like animal substance, acrid and piquant and similar to the smell of rat urine, and turning litmus paper strongly blue. Tests were conducted to verify that the basic reaction was not due to ammonia. All these were clear signs of the presence of a volatile alkaloid, probably coniine or nicotine. One sample of the liquid was treated with sulfuric acid and another with nitric acid; if the alkaloid were coniine, its sulfate or nitrate would color the solution purple red; if it was nicotine, no color change would be observed. Similar tests indicated that nicotine was present in the entire organ samples received from the court. Stas believed that all his results indicated clearly that the deceased had died of nicotine poisoning, a kind of poisoning that no one had reported previously. All these tests were made in the presence of Charles Wauwermans, a court clerk appointed by the judge to serve as witness of all the work done by Stas. The judge, the clerk, and other persons tasted a sample of the material separated by Stas and declared that it tasted like tobacco (Stas, 1851).

Stas report to the judge contained a detailed description of the exams and results conducted on the different samples that he had received from the court. The answer to the questions was as follows: (a) the deceased had clearly ingested poisonous materials; (b) these materials were nicotine and vinegar (one of the most violent poisons known); (c) there were no signs of ingestion of sulfuric acid; (d) although it was impossible to determine the ingested weight of both poisons, the amount of nicotine found in the stomach of Fougnies was more than enough to kill a very strong man; and (e) the alterations presented by the different organs examined coincided with those observed in animals poisoned by a very large dose of nicotine.

According to Stas the nicotine had been ingested first and then the victim had been laid on its back with his head turned to the right. Afterwards, tetanus convulsions had taken place and continued until death. The vinegar had been administered after death and after the poison had produced its cauterizing action on all the organs it had come into contact. Stas remarked that it was not his duty to explain why the vinegar had been added afterwards (Stas, 1851).

In an additional requisition, the judge ordered Stas to analyze samples of the clothes belonging to the count as well of the wooden floor of the dining room of the Bocarmé castle. Stas found that both materials presented clear signs of blood and nicotine. In addition, it was clear that the floor had been repeatedly washed and strongly brushed (Stas, 1851). Stas' pathological work led to the conviction and execution of Hyppolyte Visart de Bocarmé. This particular work of Stas is probably one of the best proofs of his extraordinary ability as chemical analyst and careful researcher.

Detection of alkaloids in cases of poisoning

Stas believed it was possible to detect in a suspected liquid the presence and identity of all the known alkaloids (e.g. coniine, nicotine, morphine, codeine, noscapine, strychnine, brucine, cevadine, colchicine, delphin, emetine, solanine, aconitine, atropine, hyoscyamine, etc.), in whatever state they were present. In a publication of the subject he described a general procedure for achieving this goal. His method was very similar to the one employed for extracting these alkaloids from the vegetables that contained them, except in the manner of setting them free and separating them with different solvents (Stas, 1853).

It was known that alkaloids formed acid salts, soluble in water and alcohol, and that their aqueous solution could be decomposed to liberate the alkaloid momentarily or permanently. Stas added that he had found "that the alkaloids could always be extracted from the solution when using an appropriate solvent in sufficient quantity". In few words, the problem reduced to separating the alkaloid from the accompanying foreign matters and finding a base, which would liberate it and leave it in solution so that it could be extracted with ether. The foreign materials were easily eliminated by successive washes with water and alcohol and the alkaloids set free by means of sodium or potassium bicarbonate or by mineral alkalis. Stas warned that animal carbon should not be used in forensic researches because it also adsorbed the alkaloids (Stas, 1853).

Stas' procedure for testing the presence of alkaloids in the contents of the stomach or intestines, was the following: (a) The tested matter, finely divided if necessary, was first mixed with twice its weight of pure and very strong alcohol; (b) the liquid suspension was mixed with 0.5 to 2 grams of tartaric or oxalic acid and then heated in a flask to 60° or 75 °C; (c) after complete cooling, the mixture was filtered, the insoluble residue washed with strong alcohol, and the filtered liquid evaporated under vacuum; (d) once the alcohol had been eliminated, the residue was extracted with cold anhydrous alcohol, and the alcohol evaporated at room temperature under vacuum until almost dryness; (e) the acid residue was now dissolved in the smallest possible quantity of water and neutralized by adding powdered sodium or potassium bicarbonate in small portions until a fresh quantity produced no further effervescence of CO.; and finally (f) the mixture was treated with four or five times its bulk of pure ether, left to settle, decanted, and left to dry in a very dry place (Stas, 1853).

The following stages depended on whether the alkaloid contained in the suspected matter was liquid and volatile, or solid and fixed. For example, if the suspected matter was a solid or fixed alkaloid, the evaporation of the ether resulting from the treatment of the acid matter, could leave or not a residue, containing an alkaloid. If it did, the alkaloid was freed by addition of a solution of KOH or NaOH, followed by agitation. Evaporation of the ether usually left a colorless milky acid liquid, holding solid matters in suspension, having a disagreeable odor. The residue was then treated with alcohol and the filtered solution left to evaporate spontaneously. The resulting alkaloid was purified by extraction with acidulated water, followed by neutralization with potassium carbonate, extraction with alcohol, and evaporation. The identity of the resulting crystalline alkaloid was carried out by standard methods, particularly by its properties (Stas, 1853).

TABLE 1
Comparison of atomic masses

	Usual	Stas		
Silver	108	107.943		
Chlorine	35.5	35.46		
Potassium	39	39.13		
Sodium	23	23.05		
Ammonium	18	18.06		
Nitrogen	14	14.041		
Sulfur	16	16.037		
Lead	103.5	103.453	(Synthesis of lead sulfate)	
Lead	103.5	103,460	(Synthesis of lead nitrate)	

TABLE 1
Comparison of atomic masses

	Oxygen = 16.000	Hydrogen = 1
Silver	107.930	107.660
Nitrogen	14.044	14.009
Bromine	79.952	79.750
Chlorine	35.457	35.368
Iodine	126.850	126.533
Lithium	7.022	7.001
Potassium	39.137	39.040
Sodium	23.043	22.960
Oxygen	16.000	15.960

FIGURE 1:
Jean-Servais Stas (1813-1891)

REFERENCES

Boussingault, J. B. (1834). Recherches sur la Composition de l'Atmosphère. *Ann. Chim. Phys., 57*, 148-182

Döbereiner, J. W. (1832). Bildung des Sauerstoff-Aethers durch Atmosphärische Oxidation des Alkohols. *Schweigger J., 64*, 466-468.

Dumas, J. B., & Stas, J. S. (1840a). Notice sur l'Action des Alcools sur les Alcalis. *Compt. Rendus, 10*, 260-264.

Dumas, J. B., & Stas, J. S. (1840b). Second Mémoire sur les Types Chimiques. *Ann. Chim. Phys.* [3], *73*, 113-166.

Dumas, J. B., & Stas, J. S. (1840c). Recherches sur les Véritable Poids Atomique du Carbone. *Compt. Rendus, 11*, 991-1008.

Dumas, J. B., & Stas, J. S. (1841). Recherches sur les Véritable Poids Atomique du Carbone. *Ann. Chim. Phys.* [3], ., 5-59.

Liebig, J. (1833). Über Acetal (Sauerstoffäther), Holzgeist und Essigäther. *Ann. Pharm.*, ., 25-37.

Malaguti, F. J. (1838). Note sur le Formométhylal. *Compt. Rendus, 7*, 491-492.

Morley, E. W. (1892). Jean Servais Stas. *J. Am. Chem. Soc., 14*, 173-189.

Spring, W. (1894). Notice sur la Vie et les Travaux de Jean-Servais Stas. *Ann. Roy. Acad. Belgique, 39-40*, 217-376.

Stas, J. S. (1838). Recherches Chimiques sur la Phloridzine (No. 1), *Ann. Chim. Phys., 69*, 367-401.

Stas, J. S. (1839). Recherches Chimiques sur la Phloridzine (No. 2). *Bull. Acad. Roy. Sci., Bruxelles, 6*, 103-108.

Stas, J. S. (1841). Note sur l'Action de l'Hydrogène sur quelques Matières Chlorées. *Bull. Acad. Roy. Sci., Bruxelles,* 8, 162-164.

Stas, J. S. (1842). Analyse de l'Air. *Compt. Rendus, 14*, 297-298.

Stas, J. S. (1847). Recherches Chimiques sur les Propriétés et la Composition de l'Acetal. *Ann. Chim. Phys.* [3], *19*, 146-158.

Stas, J. S. (1849). Recherches sur les Véritable Poids Atomique du Carbone. *Bull. Acad. Roy. Sci,, Bruxelles, 16*, 9-34.

Stas, J. S. (1850). Note sur les Liquides de l'Amnios et de l'Allantoïde. *Compt. Rendus*, 31, 629-630.

Stas, J. S. (1851). Recherches Médico-Légales sur la Nicotine, suivies de quelques Considérations sur la Manière Générale de Déceler les Alcalis Organiques dans les Cas d'Empoisonnement. *Bull. Acad. Roy. Sci., Bruxelles, 11*, 202-216.

Stas, J. S. (1853). Considérations sur la Manière Générale de Déceler les Alcalis Organiques dans les Cas d'Empoisonnement. *J. Pharm.* [3], *22*, 281-288.

Stas, J. S. (1860). Recherches sur les Rapports Réciproques des Poids Atomiques. *Bull. Acad. Roy. Sci., Bruxelles, 10*, 208-336.

Stas, J. S. (1866). Nouvelle Recherches sur les Lois de Proportions Chimiques, sur les Poids Atomiques et leur Rapports Mutuels. *Ann. Chim. Phys.* [4], *9*, 215-243.

Stas, J. S. (1867a). On the Invariableness Between the Ratios of the Weights of the Elements Forming Chemical Compounds. *Chem. News, 15*, 307-308.

Stas, J. S. (1867b). On the Action of Chlorine on Carbonate of Silver. Preparation of Chlorate of Silver. *Chem. News.,* 16, 79-81.

Stas, J. S. (1868a). On the Manufacture of Glass for Vessels Employed in Chemical Researches. *Chem. News, 17*, 1.

Stas, J. S. (1868b). Preparation of Iodic Acid and Iodate of Potassium. *Chem. News, 18*, 73.

Stas, J. S. (1868c). On the Action of Sulfurous Acid on Compounds of Silver. *Chem. News, 18*, 86-87.

Stas, J. S. (1871). Recherches de Statique Chimique. Des Phénomènes qui Passent dans la Précipitation Mutuelle des Solutions Diluées de Sels d'Argent par les Acides Chlorhydrique, Bromhydrique, Iodhydrique, et les Chlorures, Bromures et Iodures. *Compt. Rendus, 73*, 998-1002.

Stas, J. S. (1880). La Science et l'Imagination. *Bull. Acad. Roy. Sci., Bruxelles, 50*, 375-422.

Stas, J. S. (1890-1893a). De la Nature de la Lumière Solaire. *Mém. Acad. Roy. Sci., Bruxelles, 49*(2) (posthumous); 47 pages.

Stas, J. S. (1890-1893b). De l'Argent. *Mém. Acad. Roy. Sci., Bruxelles, 49*(7) (posthumous); 168 pages.

Stas, J. S. (1890-1893c). Recherches Chimiques et Études Spectroscopiques sur Différents Corps Simples. Nouvelle Détermination du Rapport Proportionnel entre l'Argent et le Chlorure de Potassium. *Mém. Acad. Roy. Sci., Bruxelles, 49*(8) (posthumous); 246 pages.

Stas, J. S. (1894a). *Œuvres Complètes*. L. W. Spring, editor, Muquart, Bruxelles; vol 1.

Stas, J. S. (1894b). *Œuvres Complètes*. J. B. Depaire, editor, Muquart, Bruxelles; vol 2.

Stas, J. S. (1894c). *Œuvres Complètes*. L. W. Spring, editor, Muquart, Bruxelles; vol 3.

Stas, J. S., & de Hemptinne, A. D. (1843). Rapport sur un Mémoire Présenté par M. Melsens, Relatif à l'Action de l'Acide Sulfurique sur l'Acide Acétique. *J. Pharm.,* 4, 130-134.

Stas, J. S., & de Konick, L. G. (1835). De la Phloridzine. *Bull. Acad. Roy. Sci., Bruxelles, 2*, 5-6.

Timmermans, J. (1938). Jean Servais Stas. *J. Chem. Educ.*, *15*, 353-357.